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<b>(54) Title:</b> WATER-RESISTANT STARCH-PROTEIN THERMOPLASTICS  <b>(57) Abstract</b>  The present invention provides a biodegradable thermoplastic composition made of native or modified starch that is externally cross-linked to a protein using an aldehyde or epoxide cross-linking agent. The compositions may be used to make extruded or molded articles that have a high level of water-resistance and physical strength.		

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**WATER-RESISTANT STARCH-PROTEIN THERMOPLASTICS****BACKGROUND OF THE INVENTION**

5           Various biodegradable thermoplastic compositions have been developed in an attempt to replace non-degradable petroleum-based thermoplastics for the manufacture of extruded and/or molded articles such as films, utensils, containers and other packaging  
10 articles. Several of these compositions have been formulated using a starch such as a destructured starch, which has had its molecular structure modified, such as by melting or by acid treatment. Although such starch compositions are biodegradable, they also tend to  
15 readily absorb moisture from humid air or direct contact with water. This causes the moisture content of a molded article to increase and the article to lose its dimensional stability, and tear or collapse.

          In an attempt to improve the structural  
20 stability of articles made from destructured starch compositions, other ingredients have been included in the formulations. For example, European Patent Application No. 0,327,505 to Warner-Lambert Company (published August 9, 1989) discloses a blended polymeric  
25 material made of a melt of destructured starch and a water-insoluble synthetic thermoplastic polymer such as polyolefin or a polyester. In British Patent Application No. 2,214,920 to Warner-Lambert Company (published September 13, 1990), a moldable polymeric  
30 composition is formed by heating together zein with starch that has been destructured by acid treatment. Organosilanes are used to further modify the surface of the starch to improve its compatibility with the zein.

          Unmodified starches have also been combined  
35 with protein to provide moldable, biodegradable thermoplastic compositions. For example, Nakatsuka et al. (U.S. Patent No. 4,076,846; issued February 28, 1978) discloses an edible binary protein-starch molding composition containing a salt of a natural protein

(i.e., casein), an unmodified, high amylose starch material, an edible plasticizer (i.e., sorbitol), and a lubricant (i.e., a fatty acid polyol ester), and having a final water content of about 10-40%. The composition is molded, for example, by extrusion through a die, into an article having a water content of about 5-30 wt-%.

A disadvantage of these starch-based plastics is that the molded articles made from such compositions have a high tendency to absorb water, which causes the articles to lose mechanical strength and to disintegrate quickly.

Therefore, an object of the invention is to provide a starch-based thermoplastic material that can provide articles that have an increased level of water-resistance in that they will tolerate exposure to water over an extended period of time with minimal or no disintegration.

#### SUMMARY OF THE INVENTION

The present invention provides a starch and protein-based biodegradable thermoplastic composition that may be used to make extruded, molded or otherwise pressure-formed articles.

The composition comprises a cross-linked mixture of a native or modified starch in intimate admixture with a protein such as zein, gluten, soybean protein, and the like. A cross-linking agent, as for example, an aldehyde such as glutaraldehyde and formaldehyde, an epoxide such as epichlorohydrin, or other suitable cross-linking agent, is used to bind the starch and protein together.

The invention unexpectedly provides a plastic material that may be molded or otherwise shaped to provide a biodegradable article that has an increased level of water-resistance and improved mechanical properties, such as tensile strength and hardness, over articles made from current starch-protein thermoplastic

materials. Although the articles made from the composition of the invention will degrade over time when exposed to moisture, such as from the atmosphere, the package contents, or from submersion in water or other direct contact with water, the articles of the invention have a higher resistance to such degradation and will remain substantially intact for a more extended period of time than articles made from other starch-protein-based thermoplastics.

10           The cross-linked starch-protein composition of the invention may be produced by dissolving protein in a compatible solution, adding the cross-linking agent to the mixture, and then adding the starch. Alternatively, the starch and protein may be combined in the solution, and the cross-linking agent subsequently added. The starch, protein and cross-linking agent are combined in solution to provide a dough-like material, or filtered or centrifuged to remove excess liquid to provide a solid residue, and then dried to a predetermined moisture content. The dried materials may then be molded into various shaped articles according to techniques known in the art, as for example, by compression molding, injection molding, and the like.

#### 25           DETAILED DESCRIPTION OF THE INVENTION

The thermoplastic compositions of the invention comprise a natural or modified starch, a protein and a cross-linking agent such as an aldehyde, an epoxide or other suitable agent. The reaction of the cross-linking agent with the starch and protein causes the formation of starch-protein linkages, starch-starch linkages, and protein-protein linkages.

30           The compositions of the invention are formed by combining the protein, starch and cross-linking agent in a solution such as aqueous methanol, ethanol, isopropanol, buffer solutions, and the like, and then reducing the water content to a predetermined amount.

The present compositions are useful as molding materials for forming articles of various shapes, forms and sizes. It was unexpectedly found that articles formed from the present compositions have an increased level of water-resistance resulting in improved structural stability and resistance to disintegration due to exposure to water, as compared to articles formed from other types of starch-protein compositions.

#### 10 Starches

The composition of the invention includes a natural or modified starch that is capable of being cross-linked together by means of a suitable cross-linking agent to form a starch to starch cross-link, and with protein to form a starch to protein cross-link. The composition contains an amount of starch in combination with the protein that is effective to provide a cross-linked starch-protein thermoplastic composition that can be molded into an article that has the desired level of structural stability and water resistance.

Native or natural starches that are useful according to the invention include, for example, starch derived from corn, potato, tapioca, rice, wheat, rye, oats, barley, sorghum, mung bean, sweet potato, high amylose corn, waxy corn (maize), waxy rice, and the like. Alternatively, the starch can be presented in the form of a cereal flour, such as milled wheat, oats, corn, rye and the like.

Starches, that have been chemically modified, as for example, by acetylation, oxidation, hydroxypropylation, cationization, phosphorylation, cross-linking or other like process, may also be used according to the invention. Examples of chemically-modified starch materials suitable for use in the present composition include, but are not limited to, aluminum starch octenylsuccinate, carboxymethyl starch,

hydroxyethyl starch, hydroxypropyl starch, methyl starch, ethyl starch, methyl hydroxyethyl starch, ethylhydroxy-propyl starch, starch phosphate, starch acetate, starch propionamide, starch maleate, cationic starch, cross-linked starch, and the like.

Physically-modified starches may also be used, such as a pregelatinized starch, or a granular, cold water-soluble starch as described, for example, in U.S. Patent No. 5,057,157 to Jane, et al. (issued October 15, 1991) and U.S. Patent No. 4,465,702 to Eastman, et al. (issued August 14, 1984), the disclosures of which are incorporated by reference herein.

The starch material of the composition may be a normal starch (about 20-30% by weight amylose), waxy starch (about 0-8% by weight amylose), or a high-amylose starch (greater than about 50% by weight amylose).

### Proteins

Natural starches and modified starches are greatly affected by water which may cause rapid disintegration of the plastics. The composition of the present invention contains an amount of protein effective to provide a molded article having a level of structural stability and water resistance such that the article, when exposed to water, such as from humid air or from direct contact with water, will remain essentially intact without significant deterioration for a period of at least about 24 hours, preferably about 48 to 72 hours, more preferably about 14 days. Preferably, the composition contains a starch to protein weight ratio of about 95:5 to about 50:50, more preferably about 90:10 to about 70:30.

Suitable proteins that may be used to form the composition of the invention include proteins that are capable of being externally linked by conventional cross-linking agents to the starch that is included in

the composition. Preferably, the protein component is a water-resistant, or hydrophobic, protein.

The protein component may be derived from plants, animals and/or microorganisms. Animal-derived proteins that are suitable for use in the present composition include, for example, casein derived from milk, albumin derived from blood or egg, collagen, gelatin, keratin, and other like protein-containing substances. Suitable plant-derived proteins include, for example, gluten, zein, soybean protein, hordein, kafirin, avenin, and the like. Microorganisms, such as beer yeast and baker's yeast, among other organisms, may also be used in the present compositions.

15 **Cross-Linking Agent.**

According to the invention, a cross-linking agent is combined with the protein and starch components to internally bond the protein together in a protein to protein linkage, to internally bond the starch together in a starch to starch linkage, and to externally link the starch to the protein in a starch to protein linkage. The inclusion of a cross-linking agent into the present compositions provides a moldable starch-protein composition that may be molded or otherwise formed into an article that has a high level of water resistance and improved mechanical properties over articles formed from other starch-based plastics which tend to disintegrate within a short period of time when exposed to water.

Suitable cross-linking agents according to the invention, include aldehydes such as glutaraldehyde, formaldehyde, glyoxal, acetaldehyde, acrolein, glyceraldehyde, furfuraldehyde, malonic dialdehyde, succinic dialdehyde, adipic dialdehyde, starch dialdehyde, and the like; epoxides such as epichlorohydrin, 3-chloro-1,2-epoxypropane, 3-bromo-1,3-epoxypropane, 3-chloro-1,2-epoxybutane, 3-4-dichloro-



1,2-epoxybutane, 4-chloro-1,2-epoxypentane, chloroepoxyoctanes, and the like; polyepoxides such as vinyl cyclohexane dioxide, butadiene dioxide, and the like; and other starch-protein cross-linking agents such as phosphorus oxychloride, soluble metaphosphates, a mixture of adipic anhydride and acetic anhydride, and the like.

Preferably, the cross-linking agent will be present at about 0.1 to 5.0 wt-%, based on the total weight of solids in the composition.

#### Other Additives

To facilitate processing of the starch-protein compositions of the invention and to increase the flexibility and toughness of the molded article, a minor but effective amount of a compatible plasticizer may also be included in the present composition. Plasticizers that may be used according to the invention, include low molecular weight hydrophilic organic compounds such as di- or polyhydric alcohols and derivatives thereof, as for example, glycerol, glycerol monoacetate, diacetate or triacetate, sorbitol, sorbitan, mannitol, maltitol, ethylene glycol, diethyl glycol, propylene glycol, polyvinyl alcohol, and the like; sodium cellulose glycolate, cellose methyl ether, and the like; sodium diethysuccinate, triethyl citrate, and the like; and polyalkylene oxides such as polyethylene glycols, polypropylene glycols, polyethylene propylene glycols, polyethylene glycol fatty acid esters, and the like. The amount of plasticizer that would be included in the composition is about 0.2 to 20 wt-%, preferably about 0.5 to 10 wt-%, based on the total weight of the solids in the composition.

The composition may further contain a minor but effective amount of a lubricating agent effective to provide a mold- or dye-lubricating effect when the

composition is molded into the desired article, for example, by aiding in the release of the molded article from the mold. Examples of suitable lubricants that may be used in the compositions, either alone or in  
5 combination with another lubricant, include mono- and diglycerides, and fatty acids, preferably saturated fatty acids; phospholipids such as lecithin; phosphoric acid-derivatives of the esters of polyhydroxy compounds; vegetable oil, preferably hydrogenated forms; animal  
10 fats, preferably hydrogenated forms to prevent thermal oxidation; and petroleum silicone and mineral oils. The amount of lubricant contained in the composition is preferably about 2 wt-% or less, more preferably about 0.1 to 1 wt-%, based on the total solids weight of the  
15 composition.

Extenders, for example, water soluble polysaccharides such as methylcellulose, hydromethylcellulose, and microcrystalline cellulose, and synthetic polymers such as poly(acrylic acids),  
20 poly(methacrylic acids), poly(vinyl acetates), poly(vinyl alcohol), and poly(vinyl acetate phthalate), may also be included in the composition. Preferably, an extender is included in the composition in an amount of about  $\leq 50$  wt-%, more preferably about 3 to 20 wt-%,  
25 based on the total solids weight of the composition.

A compatible antimicrobial agent such as a fungicide or bactericide may also be included in the composition in an amount effective to prevent growth of fungi, bacteria and the like, in or on the compositions  
30 or an article formed from the compositions. The antimicrobial agent should not induce undesirable interactions or chemical reactions between the components of the composition.

The compositions may further include a coloring  
35 agent. Coloring agents, suitable for use in the present compositions include, for example, azo dyes such as Bismarck Brown 2R and Direct Green B; natural coloring

agents such as chlorophyll, xanthophyll, carotene, and indigo; and metallic oxides such as iron or titanium oxides. The coloring agent may be included in the composition at a concentration of about 0.001 to 10 wt-%, preferably about 0.5 to 3 wt-%, based on the total solids weight of the composition.

The present starch-protein thermoplastic composition may be comprised entirely of ingredients that may be consumed by a human or other mammal. In that case, the article formed from the composition would be biodegradable as well as edible by a mammal. An edible composition according to the present invention, would comprise, for example, a natural, unmodified starch such as corn starch, and/or a modified food starch such as hydroxypropylated starch, a natural protein such as zein, soy protein, gluten or casein, and a cross-linking agent such as starch dialdehyde, or a mixture of adipic and acetic anhydrides. An edible composition may further include an edible plasticizer such as sorbitol, a lubricating agent such as lecithin or mineral oil, an extender such as microcrystalline cellulose, and/or an antimicrobial agent such as methyl paraben. An effective amount of an edible flavoring agent such as cocoa, vanillin, fruit extracts such as strawberry and banana, and the like, may also be included to enhance the taste of an edible composition.

To produce the compositions of the invention, an effective amount of starch and protein are combined in an amount of a solution compatible with the protein and starch and other components of the composition, as for example, aqueous methanol, ethanol, a buffer solution such as an acetate or phosphate buffer, and the like, to form a suspension. An amount of a suitable cross-linking agent effective to provide cross-linking of the starch to the protein, is added to the protein-starch mixture.

The compositions may be produced by (a) dissolving an effective amount of a protein in a compatible solution, (b) adding to the protein solution an effective amount of a suitable cross-linking agent, and (c) combining the protein/cross-linking agent mixture with an effective amount of a starch material. Alternatively, the cross-linking agent may be added to a mixture of the protein solution and the starch. A preferred composition may be prepared by combining about 0.5-5 parts by weight protein and about 5-9.5 parts by weight starch in about 6-15 parts solution to form a mixture, to which about 0.01-0.5 parts by weight cross-linking agent may be added.

The starch/protein/ cross-linking agent suspension may be blended for a suitable amount of time to provide a mixture that has a dough-like consistency. Optionally, to facilitate processing, excess liquid and/or cross-linking agent may be removed from the suspension, for example, by decanting, centrifuging, filtering, and the like. The mixture is then dried to a predetermined water content. Preferably, the final water content of the dried dough mixture is about 3 to 35 wt-%, more preferably about 6 to 20 wt-%. To facilitate processing, the mixture may require the addition of moisture, which may be added, for example, by storing the mixture in a humid chamber or by adding moisture directly to the mixture while mixing. Optionally, the mixture may be extruded with or without heating into a rod shape and granulated into chips. To facilitate processing by extrusion, the material may include an effective amount of water or other solvent, preferably about 15% to 30%.

Alternatively, the starch/protein/cross-linking agent suspension may be filtered to remove excess liquid, and the residue dried or moistened to a suitable moisture content, preferably about 3 to 35 wt-%, more preferably about 6 to 20 wt-%. The dried residue may be

further processed, as for example, by crushing or grinding the residue into a powder, granules and the like.

A preferred composition prior to molding, contains about 5 to 50 wt-% protein, more preferably about 10 to 30 wt-%, with hydrophobic proteins such as zein or gluten being preferred; about 50 to 95 wt-% starch, more preferably about 70 to 90 wt-%, with natural corn, potato, or wheat starch being preferred; and about 0.1 to 5 wt-% cross-linking agent, more preferably about 0.5 to 1.0 wt-%, with formaldehyde and glutaraldehyde being preferred; the wt-% of the components being based on the total dry weight of the composition. The preferred composition prior to molding has a moisture content of about 3 to 35 wt-%, more preferably about 6 to 20 wt-%.

The cross-linked starch-protein composition of the present invention may be formed into a desired article according to techniques known in the art for molding thermoplastic materials. For example, the composition may be shaped by compression molding wherein direct pressure is applied using a hydraulic press on an amount of the composition contained in a cavity; by injection molding wherein an amount of the plastic composition in melted form is forced into a mold and maintained under pressure until cool; by blow molding wherein a tube of the thermoplastic composition is extruded into a mold and air pressure is applied to the inside of the tube to conform it to the mold and form a hollow article; and by other methods such as rotation molding, transfer molding, extrusion molding, vacuum forming, pressure forming, and inflation molding.

The composition of the invention may be molded to provide articles of varying shapes, sizes and dimensions, that are useful in a variety of applications. For example, the composition may be molded into an article such as a sheet, film, capsule,

tray, bottle, tubing or the like. The composition of the invention may be molded or extruded to provide foamed products such as packaging, loose fills, foamed dishes and cups, and the like. Residual water in  
5 the composition may be suitably used as a blowing agent. The articles may be used for packaging another article or substance such as foods, drugs and the like, that contain moderate amounts of water. As a further example, the compositions may be molded into dishware  
10 such as a cup or a plate, flatware such as a knife, fork or other eating utensil, or other like articles.

The compositions of the invention are useful for providing articles that are biodegradable, but with improved water-resistance so that the article will  
15 remain structurally intact for an extended period of time upon exposure to water. Apart from being biodegradable, the compositions may be comprised entirely of components that are edible by a human or other mammal so that articles molded from such  
20 compositions may be safely consumed by the mammal. Such edible compositions would be useful for making, for example, a packaging article that may be consumed by the user along with the package contents, dishes and flatware that may be ingested following a meal, a food  
25 article for consumption by a human or other mammal such as a snack food or a domestic pet or other animal food, or other articles where consumption of the article is desired.

The invention will be further described by  
30 reference to the following detailed examples. These examples are not meant to limit the scope of the invention that has been set forth in the foregoing description. It should be understood that many variations and modifications may be made while remaining  
35 within the spirit and scope of the invention.

Example 1**Corn Starch-Zein Thermoplastic  
formed without Cross-Linking Agent**

5           A starch-protein thermoplastic composition was formulated by treating corn starch with a zein-aqueous alcohol solution without the addition of a cross-linking agent. The starch thus treated had a layer of zein evenly coated on the surface, which increased water  
10 resistance. The suspension was mixed to a dough-like consistency, dried, and then compression molded into a standard test article.

          Zein (1 part by dry weight; Sigma Chemical Co., St. Louis, Mo.) was dissolved in 75% aqueous methanol  
15 (6.4 parts by weight) by mechanically agitating for 15 minutes. A commercially-available corn starch (75% amylopectin, 25% amylose; 7.3 parts by dry weight) was added to the zein-alcohol solution. The resulting zein-corn starch suspension was mixed together by agitating  
20 with a dough mixer at room temperature (25°C) to yield a homogenous mixture that had a dough-like consistency. The dough mixture was dried overnight (about 16 hours) in a convection oven at 50°C until the moisture content reached 8-10%. After cooling, the solid material was  
25 ground to coarse granules using a coffee mill. The granules were then compression molded using a compression molding press (Wabash Metal Products, Inc., Wabash, IN) at 160°C, 5,000 compression (psi) to form a standard dog-bone-shaped article as described in the  
30 American Society for Testing and Material (ASTM D638-86), the disclosure of which is incorporated by reference herein.

          The tensile properties of the molded articles were tested according to ASTM standard method D638-86,  
35 the disclosure of which is incorporated by reference herein, using an Instron Universal Testing System (Model 4052, Canton, MA). Testing speed was 10mm/second. The

tensile strength of the article was less than 1.0 kg/mm<sup>2</sup>, and the percent elongation at break was less than 2.0%.

The molded articles were submersed in distilled water at room temperature (25°C) for 24 hours. Water  
5 absorption of the molded articles was tested at 2 hours and at 24 hours according to ASTM standard method D570-81, the disclosure of which is incorporated by reference herein. The water absorption of the molded article was  
10 10.9% after 2 hours, and the immersed articles became increasingly swollen and gradually cracked during the 24-hour period. Within 48 hours, the articles had substantially disintegrated.

#### Example 2

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##### **Corn Starch-Zein Thermoplastic Formed without Cross-Linking Agent**

Starch-protein compositions without a cross-  
20 linking agent were prepared as described in Example 1. Zein (1 part by weight) was dissolved in 75% aqueous methanol (6.4 parts by weight), and combined with 4.9 parts by weight corn starch. The tensile strength of the molded article formed from the composition was 1.7  
25 kg/mm<sup>2</sup>, and the percent elongation at break was 1.4%. The water absorption of the molded article was 10.3% after 2 hours of being submerged in distilled water at room temperature (25°C). The immersed articles became  
30 increasingly swollen and gradually cracked during the 24 hour period. Within 48 hours, the articles had substantially disintegrated.

#### Example 3

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##### **Corn Starch-Zein Thermoplastic formed with Formaldehyde as the Cross-Linking Agent**

Starch-protein compositions were prepared as described in Example 1, except that an aqueous  
40 formaldehyde solution (37%) was mixed with a protein-aqueous methanol or a protein-aqueous ethanol solution,



and then the corn starch was added. The formulations of the compositions that were prepared are shown in Table 1 below.

Each of the suspensions were mixed to a dough-  
5 like consistency, dried to a solid that had a moisture  
content of 8-10%, ground to granules, and compression  
molded into a D638-86 ASTM standard bone-shaped article,  
as described in Example 1. The tensile strength  
(kg/mm<sup>2</sup>), % elongation, yield strength, and % water  
10 absorption were measured for each of the molded  
articles. The results are shown in Table 1 below.

Table 1<sup>1</sup>

Zein <sup>2</sup> (%)	Corn starch (%)	Formal- dehyde <sup>3</sup> (%)	Tensile strength <sup>4</sup> (kg/mm <sup>2</sup> )	Percent Elon- <sup>4</sup> gation	Yield Strength (kg/mm <sup>2</sup> )	% Water Absorption	
						2 hrs.	24 hrs.
10	90	0.2	1.3(0.2)	1.2(0.4)	0.29(0.05)	9.5(1.4)	28.5(1.1)
10	90	0.4	1.2(0.2)	1.6(0.2)	0.25(0.11)	8.1(0.6)	26.4(1.5)
10	90	0.53	0.8(0.2)	0.9(0.1)	0.14(0.06)	7.5(0.7)	24.4(2.4)
10	90	0.8	0.9(0.2)	1.2(0.2)	0.15(0.11)	7.1(0.2)	22.7(0.9)
10	90	1.0	1.6(0.1)	1.3(0.1)	0.36(0.05)	8.2(1.0)	27.8(2.9)
12	88	0.40	1.7(0.2)	1.5(0.2)	0.34(0.04)	6.9(0.2)	23.1(1.3)
12	88	0.66	1.7(0.3)	2.4(0.5)	0.32(0.05)	6.2(0.3)	19.2(0.5)
12	88	0.80	1.7(0.2)	1.7(0.2)	0.32(0.02)	7.1(0.5)	21.7(1.6)
12	88	1.64	2.4(0.2)	2.7(0.5)	0.41(0.02)	6.7(0.3)	20.1(0.6)
17	83	0.8	2.9(0.3)	2.5(0.5)	0.45(0.03)	6.0(0.1)	19.0(0.1)
17	83	2.0	2.5(0.3)	2.4(0.4)	0.43(0.07)	6.7(0.3)	23.9(1.1)
25	75	0.8	1.6(0.2)	1.6(0.1)	0.31(0.06)	7.3(0.3)	24.4(1.4)
30	70	0.8	2.3(0.3)	2.0(0.3)	0.40(0.01)	6.5(0.1)	22.5(0.2)

<sup>1</sup> Numbers are averages of the test data of five ASTM standard articles.  
( ) = Standard Deviation.

<sup>2</sup> 75% aqueous methanol (1:1.3 = 75% methanol:total dry weight of the solid mixture) was used to dissolve zein.

<sup>3</sup> Percent weight of formaldehyde is calculated on the basis of total dry weight of zein and corn starch.

<sup>4</sup> Tensile strength and percent elongation were obtained at the breakage of the specimen.

The tensile strength and yield strength of the article showed an increase with an increasing protein content from 10 to 17%.

The molded articles were submersed in distilled  
5 water at 25°C. After 24 hours, the articles became structurally weak and soft due to swelling from water uptake. The articles remained substantially intact structurally for a period of 14 days.

The articles molded from the formaldehyde  
10 cross-linked compositions in methanol had a higher tensile strength, greater yield strength, and a lower % water absorption, both at 2 hours and at 24 hours, than the articles formed with the non-cross-linked composition of Example 1. The lower % water absorption  
15 of the articles formed from the cross-linked compositions demonstrates that internally and externally cross-linking the macromolecules with a formaldehyde cross-linker provides a rigid network structure which  
increased the water-resistance of the formed articles.

20

#### Example 4

##### **Corn Starch-Zein Thermoplastic formed with Glutaraldehyde as the Cross-Linking Agent**

25 Zein-corn starch compositions were formulated according to the procedure outlined in Example 3, except that a glutaraldehyde solution (25%) was used as the cross-linking agent in place of the 37% formaldehyde solution. Formulations of the composition and the  
30 results of the tests performed on the standard articles formed from the compositions are shown in Table 2 below.

Table 2<sup>1</sup>

Zein <sup>3</sup> (%)	Corn starch (%)	Glutaral- dehyde <sup>2</sup> (%)	Tensile strength <sup>4</sup> (kg/mm <sup>2</sup> )	Percent Elon- <sup>4</sup> gation	Yield Strength (kg/mm <sup>2</sup> )	% Water Absorption	
						2 hrs.	24 hrs.
10	90	0.25	1.2(0.1)	1.2(0.2)	0.30(0.05)	10.1(0.4)	disintegrated
10	90	0.5	1.7(0.6)	1.8(0.3)	0.36(0.08)	7.7(0.2)	32.3(2.5)
10	90	1.0	1.6(0.2)	1.6(0.4)	0.33(0.03)	7.0(0.3)	22.6(0.6)
10	90	1.5	2.2(0.5)	1.8(0.6)	0.47(0.02)	6.6(0.1)	21.0(0.4)
10	90	2.0	2.5(0.3)	2.0(0.4)	0.45(0.03)	7.9(0.1)	26.1(0.2)

<sup>1</sup> Numbers are averages of the test data of five ASTM standard articles.  
( ) = Standard Deviation.

<sup>2</sup> 75% aqueous methanol (1:1.3 = 75% methanol:total dry weight of the solid mixture) was used to dissolve zein.

<sup>3</sup> Percent weight of glutaraldehyde is calculated on the basis of total dry weight of zein and corn starch.

<sup>4</sup> Tensile strength and percent elongation were obtained at the breakage of the specimen.

As in Examples 1-3, the molded articles were submersed in distilled water at 25°C. After 24 hours, the articles became structurally weak and soft due to swelling from water uptake. The articles remained substantially intact structurally for a period of 14 days.

Like the formaldehyde cross-linker, glutaraldehyde improved the physical strength and water-resistance of the starch-zein thermoplastic plastic compositions, compared to the compositions of Examples 1 and 2.

#### Example 5

#### **Other Starch-Zein Thermoplastics formed with Formaldehyde Cross-Linking Agent**

Following the procedure outlined in Example 3, thermoplastic compositions were formed with a formaldehyde cross-linking agent, and potato starch, high amylose (70% amylose) corn starch, and waxy maize starch, instead of normal corn starch (about 25% amylose) that was used in Examples 1-4. The protein and starch were combined in a 75% methanol solution (7 parts by weight). Formulations and results are shown in Table 3 below.

Table 3<sup>1</sup>

Zein <sup>2</sup> (%)	Corn starch (%)	Formal- dehyde <sup>3</sup> (%)	Tensile strength <sup>4</sup> (kg/mm <sup>2</sup> )	Percent <sup>4</sup> Elon- gation	Yield Strength (kg/mm <sup>2</sup> )	% Water Absorption 2 hrs.      24 hrs.
<u>Potato Starch</u>						
9	91	1.1	2.8(0.5)	2.8(0.3)	0.50(0.08)	13.1(0.2)    39.3(2.5)
17	83	0.8	2.0(0.5)	2.0(0.5)	0.41(0.1)	10.0(0.5)    31.3(0.9)
<u>High Amylose Corn Starch (70% Amylose)</u>						
11	89	1.4	1.5(0.5)	2.2(0.3)	0.35(0.05)	6.5(0.4)    20.8(1.1)
17	83	0.8	2.6(0.1)	2.2(0.4)	0.41(0.04)	7.2(0.2)    23.5(0.4)
<u>Waxy Maize Starch (0% Amylose)</u>						
17	83	0.8	2.5(0.2)	2.0(0.3)	0.44(0.03)	6.5(0.4)    20.4(0.9)

<sup>1</sup> Numbers are averages of the test data of five ASTM standard articles.  
( ) = Standard Deviation.

<sup>2</sup> 75% aqueous methanol (1:1.3 = 75% methanol:total dry weight of the solid mixture) was used to dissolve zein.

<sup>3</sup> Percent weight of formaldehyde is calculated on the basis of total dry weight of zein and corn starch.

<sup>4</sup> Tensile strength and percent elongation were obtained at the breakage of the specimen.

Similar to Example 1-3, the molded articles became structurally weak and soft after 24 hours of being submersed in distilled water at 25°C, but remained substantially intact structurally for a 14-day period.

The potato starch-zein mixture cross-linked with formaldehyde produced articles that were stronger and more transparent but absorbed more water than articles made from the corresponding corn starch-zein thermoplastics.

#### Example 6

##### **Corn Starch-Zein Thermoplastic with Glutaraldehyde Cross-Linking Agent** (Excess solvent and cross-linking agent removed)

A thermoplastic composition was formed by mixing zein and corn starch in a methanol solution with glutaraldehyde added as the cross-linking agent, and filtering the suspension. The resulting residue was dried and ground to a granular consistency, and molded into standard ASTM test articles.

Zein (1 part by dry weight; Sigma Chemical Co., St. Louis, Mo.) was dissolved in a mixture of 3.3 parts 25% glutaraldehyde solution and 6.7 parts absolute methanol by mechanical stirring for 15 minutes. A commercially-available corn starch (5 parts by dry weight; 75% amylopectin, 25% amylose) was added to the solution, and the mixture was stirred for 24 hours at room temperature (25°C). The reaction mixture was filtered to remove excess solvent and cross-linking agent using an aspirator with a Whatman #4 filter paper. The filtered residue was dried overnight (about 16 hours) in a convection oven at 50°C until the moisture content reached 8-10%. The starch mixture was then ground to a granular consistency using a coffee mill and then compression-molded using a compression molding press (Wabash Metal Products, Inc., Wabash, IN) at

160°C, 5,000 compression pressure (psi), to form a standard bone-shaped article in accordance with ASTM standards, as described hereinabove in Example 1.

The molded article had a tensile strength of 1.7 kg/mm<sup>2</sup>, and a percent elongation at break of 1.8%.

The article was submersed in distilled water at room temperature (25°C) for 24 hours. The article had a water absorption of 6.5% after 2 hours and 20.4% after 24 hours. The article retained its shape for more than 14 days without substantial disintegration when submerged under water at 25°C.

The physical strength and water-resistance of the articles formed with the residue from the filtered mixture were similar to the articles formed from the dough mixture.

#### Example 7

##### **Corn Starch-Zein Thermoplastic with Formaldehyde Cross-Linking Agent (Excess solvent and cross-linking agent removed)**

Following the procedure set forth in Example 6, a thermoplastic composition was formed with zein, corn starch and formaldehyde as the cross-linking agent rather than glutaraldehyde. The zein (1 part by dry weight) was dissolved in a mixture of 3.3 parts of 37% formaldehyde solution and 7.0 parts absolute methanol. The corn starch, zein and formaldehyde mixture was stirred for 1 hour at 25°C and then filtered.

The article had a tensile strength of 1.8 kg/mm<sup>2</sup>, and a percent elongation at break of 2%. The article, submerged in distilled water at 25°C, had a water absorption of 8.7% after 2 hours, and 26.4% after 24 hours.



**WHAT IS CLAIMED IS:**

1. A thermoplastic composition, comprising, in admixture:
  - (a) 50-95% by weight starch;
  - 5 (b) 5-50% by weight protein; and
  - (c) an amount of cross-linking agent effective to internally and externally link the starch and protein together to form a water-resistant biodegradable moldable thermoplastic
- 10 composition;  
the % by weight being based on the total dry weight of the composition;  
wherein the composition has a water content of about 3-35% by weight based on the total weight of the
- 15 composition.
2. The composition according to claim 1, wherein the starch is a native starch selected from the group consisting of corn starch, potato starch, wheat
- 20 starch, rice starch, waxy maize starch, waxy rice starch, high amylose corn starch, tapioca starch, oat starch, rye starch, barley starch, sorghum starch, mung bean starch, sweet potato starch, or any combination thereof.
- 25 3. The composition according to claim 1, wherein the starch is a chemically modified starch selected from the group consisting of aluminum starch octenylsuccinate, carboxymethyl starch, hydroxyethyl
- 30 starch, hydroxypropyl starch, methyl starch, ethyl starch, methyl hydroxyethyl starch, ethylhydroxypropyl starch, starch phosphate, starch acetate, starch propionamide, starch maleate, oxidized
- 35 starch, cationic starch, starch succinate, cross-linked starch, and any combination thereof.

4. The composition according to claim 1, wherein the starch is a physically modified starch that is an cold water-soluble starch, or a pregelatinized starch.
5. The composition according to claim 1, wherein the protein is a plant-derived protein selected from the group consisting of soybean protein, zein, gluten, hordein, kafirin, avenin, or any combination thereof.
6. The composition according to claim 1, wherein the protein is an animal-derived protein selected from the group consisting of collagen, casein, albumin, gelatin, keratin, or any combination thereof.
7. The composition according to claim 1, wherein the protein is derived from a microorganism selected from the group consisting of beer yeast, baker's yeast, or any combination thereof.
8. The composition according to claim 1, wherein the amount of cross-linking agent is about 0.1-5% by weight.
9. The composition according to claim 1, wherein the cross-linking agent is an aldehyde or an epoxide.
10. The composition according to claim 9, wherein the cross-linking agent is an aldehyde selected from the group consisting of glutaraldehyde, formaldehyde, glyoxal, acetaldehyde, glyceraldehyde, furfuraldehyde, malonic dialdehyde, succinic dialdehyde, adipic dialdehyde, starch dialdehyde, acrolein, or a combination thereof.

11. The composition according to claim 9, wherein the cross-linking agent is an epoxide selected from the group consisting of epichlorohydrin, 3-chloro-1,2-epoxypropane, 3-bromo-1,3-epoxypropane, 3-chloro-1,2-epoxybutane, 3-4-dichloro-1,2-epoxybutane, 4-chloro-1,2-epoxypentane, chloroepoxyoctanes, vinyl cyclohexane dioxide, butadiene dioxide, or a combination thereof.
12. The composition according to claim 1, wherein the cross-linking agent is phosphorus oxychloride, or a mixture of adipic anhydride and acetic anhydride.
13. The composition according to claim 1, further comprising a minor but effective amount of a plasticizer.
14. The composition according to claim 13, wherein the plasticizer is a polyhydric alcohol selected from the group consisting of glycerol, glycerol monoacetate, diacetate or triacetate, sorbitol, sorbitan, mannitol, maltitol, ethylene glycol, propylene glycol, polyvinyl alcohol, sodium cellulose glycolate, cellulose methyl ether, sodium alginate, sodium diethysuccinate, triethyl citrate, polyethylene glycols, polypropylene glycols, polyethylene propylene glycols, and any combination thereof.
15. The composition according to claim 1, further comprising an effective amount of a coloring agent.
16. A biodegradable thermoplastic composition produced by the process, comprising:
- (a) combining together in an effective amount of a compatible solution to form a mixture:
- (i) 50-95% by weight starch;

- (ii) 5-50% by weight protein; and  
(iii) a cross-linking agent in an amount effective to externally and internally link the starch and protein;
- 5 the % by weight of the starch and protein being based on the total dry weight of the composition;
- (b) drying the mixture to an about 3-35% by weight water content, based on the total weight of the
- 10 composition;
- wherein the starch and protein are linked by the cross-linking agent to form a cross-linked biodegradable thermoplastic composition.
- 15 17. The composition according to claim 16, wherein the mixture has a dough-like consistency prior to drying.
18. The composition according to claim 16, wherein the
- 20 starch-protein mixture is filtered or centrifuged to remove excess liquid prior to drying.
19. The composition according to claim 16, wherein the starch is corn starch, the protein is zein and the
- 25 cross-linking agent is glutaraldehyde or formaldehyde.
20. The composition according to claim 16, wherein the amount of cross-linking agent is about 0.1-5% by
- 30 weight, based on the total dry weight of the composition.
21. The composition which is produced by the process according to claim 16, further comprising molding
- 35 the composition of step (b) to yield a shaped article that is capable of remaining structurally intact without significant deterioration when

exposed to water at about 25°C for a period of about two weeks.

22. The article according to claim 20, wherein the  
5 mixture is molded into the article by injection  
molding, blow molding, compression molding, transfer  
molding, extrusion molding, vacuum molding, rotation  
molding, or expanded foam molding.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 93/02385

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl. 5 C08L3/04;      //(C08L3/04,89:00)		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl. 5	C08L ;      C08G ;      C08B ;      C08H	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,4 076 846 (NAKATSUKA ET AL.) 28 February 1978 cited in the application see column 10, line 4 - line 23 ---	1-22
X	US,A,4 585 501 (OVERHOLT S.D.) 29 April 1986 see column 2, line 41 - line 45 ---	1-22
X	EP,A,0 474 095 (BUHLER AG) 11 March 1992 see claims 1-2 see page 3, column 3, line 7 - line 18 ---	1
X	EP,A,0 095 968 (CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE) 7 December 1983 see page 5, line 29 - page 6, line 5 see example 3 --- -/-	1
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"A" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search  11 JUNE 1993		Date of Mailing of this International Search Report  05.07.93
International Searching Authority  EUROPEAN PATENT OFFICE		Signature of Authorized Officer  LENSEN H.W.M.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>a</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	GB,A,2 214 920 (WARNER-LAMBERT COMPANY) 13 September 1989 cited in the application -----	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
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